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by pyrolysis-gas chromatography and
multivariate data analysis. Applications of the
procedure

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Characterization of plastic bonded explosives by pyrolysis-gas chromatography and multivariate data analysis. Applications of the procedure

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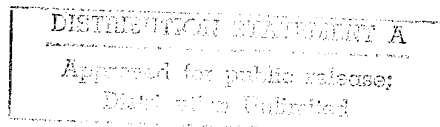*No part of this information may be disclosed to any party*

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the TNO Prins Maurits Laboratory and the
TNO Institute for Perception.

SAMENVATTING

Titel	: Karakterisering van kunststof gebonden explosieven met pyrolyse-gaschromatografie en multivariate data analyse. Toepassing van de procedure
Auteur	: M. Rietjens
Datum	: oktober 1994
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Toepassingen van de ontwikkelde procedure gebaseerd op pyrolyse-gaschromatografie (Py-GC) en principale componenten analyse (PCA) voor de karakterisering van kunststof gebonden explosieven (PBX'en) worden beschreven. Als gevolg van de moeilijkheden met de gebruikelijke normerings-methode werd een nieuwe normeringsmethode ontwikkeld en toegepast in dit onderzoek. De patronen in de "score plots" verkregen na PCA van de Py-GC resultaten bleken veel duidelijker bij het gebruik van deze nieuwe methode. PBX monsters werden onderzocht op homogeniteit, invloed van de hoeveelheid antioxydant (Flexzone) en de "crosslink" dichtheid. Het bleek dat PBX'en inhomogeen waren ondanks een intensieve menging van de bestanddelen tijdens de vervaardiging. Verouderingsexperimenten werden uitgevoerd op monsters die verschilden in de hoeveelheid Flexzone en in de "crosslink" dichtheid. Bij grotere hoeveelheden Flexzone veranderde het patroon van de GC-pieken minder. Er kon geen relatie worden gevonden tussen de stabiliteit van PBX'en en de "crosslink" dichtheid. Tenslotte werd een vergelijking gemaakt tusen Nederlandse monsters en monsters uit het Verenigd Koninkrijk en Noorwegen. Kleine verschillen tussen de monsters van de drie landen werden waargenomen.

CONTENTS

1   INTRODUCTION

Since 1989 the TNO Prins Maurits Laboratory (TNO-PML) participates for the Netherlands in IEPG TA25. This project deals with the processing of plastic bonded explosives (PBX's) based on explosives such as cyclotrimethylene-trinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) and a polymer binder. The polymer matrix consists of hydroxy terminated polybutadiene (HTPB) cured by isophorone di-isocyanate (IPDI). The binder contains also additives as plasticizers and antioxidants. Characterization of PBX's both with chemical analysis and with shock sensitivity measurements, is performed by TNO-PML within the TA 25 project.

In order to characterize the polymeric part of the PBX's the possibilities of Curie point pyrolysis gas chromatography (Py-GC) as a chemical analysis method were explored since 1987 [1]. This has led to a procedure which can be routinely applied for the characterization of PBX's [2]. After grinding, the PBX samples are pressed on a pyrolysis wire and pyrolysed. The optimum conditions of 3 parameters (temperature, pressure and mass) were determined. With these parameter settings it was possible to make a differentiation between 2 closely related PBX samples, which is a prerequisite for a good characterization. The developed procedure involves also the use of multivariate data analysis methods such as principal component analysis (PCA) to be applied on the peak areas obtained after the Py-GC analysis. An introduction of these techniques has been presented [2].

The gas chromatograms obtained after the pyrolysis of PBX's show a great variety of peak intensities with 1,3-butadiene as the most abundant peak. Before the data analysis the peak areas in the chromatograms are normalized. Up to now this was done by a commonly used normalization procedure involving the summing of all peak areas and dividing the areas by this sum. However, in situations were subtle differences have to be observed this normalization procedure gave insufficient results. Therefore, a new procedure was developed to overcome these problems, which will be described in Chapter 3.

The optimum pyrolysis conditions as well as the new normalization procedure were applied to several PBX samples. As the developed Py-GC analysis method had to be used as a quality control method, PBX's were tested on homogeneity, amount of antioxidant and crosslink density of the polymer matrix. Also the effect of aging on the last 2 types of samples was studied. Finally, samples from 2 other nations (the United Kingdom and Norway) participating in the TA 25 project were analysed.

2   EXPERIMENTAL PART

A detailed description of the equipment and procedures is presented elsewhere [2]. The pyrolysis of the PBX samples was carried out at 610 °C, applying a pressure of 5.2 tonnes and amounts of 75 µg.

The same 5 PBX samples as described before [2] were used. The PBX's were prepared at the TNO-PML according to procedures described elsewhere [3]. The samples were cured at 60 °C during one week which is sufficient for the completion of the curing reaction [4]. Their composition is shown in Table 1 together with the composition of the samples received from Norway.

Table 1   Composition and characteristics of 5 PBX samples

Code	H23	H24	R50	R63	R74	Norway
HMX	85%	85%	-	-	-	85%
RDX	-	-	85%	85%	85%	-
Flexzone[1]	-	-	0.10%	-	0.01%	-
DTBHQ[1]	0.10%	0.10%	-	0.10%	-	-
Calco[1]	-	-	-	-	-	0.10%
NCO/OH[2]	0.80	1.10	0.99	0.96	1.00	
age(yrs)	3.4	3.5	4	3	0.6	

1   Flexzone : N-phenyl-N'-cyclohexyl-p-phenylenediamine
     DTBHQ   : di-t-butylhydroquinone
     Calco   : 2,2'-methylene-bis-4-methyl-6-t-butylphenol
2   NCO/OH is the equivalence ratio of the isocyanate groups from IPDI and the OH groups from HTPB, which is a measure of the number of crosslinks per volume (crosslink density) of the polymer.

Aging experiments were performed in a climate test chamber applying a standard NATO program (cycle number 5) during one month [5]. In this program the samples were exposed to relatively high temperatures (63 °C) and humidities (75%).

The data treatment was carried out according to a new developed normalization method (see Chapter 3). For the statistical analysis the PC software package SPSS/PC+ (SPSS Inc. V3.1) was used. The GC peaks used for the data analysis are shown in Table 2.

Table 2   *GC peaks used for the data analysis*

No.	Retention time (min)	Compound
1	1.5	methane[1]
2	1.8	ethane
3	1.9	unknown
4	2.0	ethene
5	2.8	propane
6	3.9	propene
7	4.4	acetylene
8	4.7	unresolved peak[2]
9	5.0	n-butane
10	6.1	trans-2-butene
11	6.2	1-butene
12	6.5	2-methylpropene
13	6.8	cis-2-butene
14	6.9	unknown
15	7.5	unknown
16	7.7	cyclopentane
17	8.0	1,3-butadiene
18	8.7	cyclopentene
19	8.9	C_5H_{10}
20	9.0	C_5H_{10}
21	9.3	C_5H_{10}
22	9.5	C_5H_{10}
23	9.9	C_5H_8
24	10.0	methylcyclopentane
25	10.4	unresolved peak[2]
26	10.8	C_5H_6
27	10.9	n-hexane

[1] Could not be identified by GC-MS because it was overwhelmed by the peaks of NO and N_2O, but the retention time corresponded with that of methane.

[2] Due to insufficient GC resolution, the area of more than one peak was taken.

3   A NEW METHOD FOR NORMALIZING CHROMATOGRAMS

3.1   Normalization

The peak areas obtained after the Py-GC analysis of PBX samples are not only dependent on the mass of the sample but also on factors such as the area of the sample pressed on the pyrolysis wire. For the dependence on the mass of the sample a correction can easily be performed by dividing the peak areas by this mass. The other factors are more difficult to deal with [6,7]. When the sum of the peak areas of one sample is calculated this sum will be different from that calculated for another sample as well as for a duplicate. Therefore chromatograms are normalized in order to compare them [7]. The most widely used normalization procedure is summing all peak areas and dividing each peak area by this sum. This method will be abbreviated as NORM. In the Tables 3 and 4 this procedure is exemplified.

Table 3   Original peak areas in matrix notation for k samples and n peaks

	$peak_1$	$peak_2$	.	.	.	$peak_n$	Sum
$sample_1$	A_{11}	A_{12}	.	.	.	A_{1n}	S_1
	.	.	.	.	.	.	.
	.	.	.	.	.	.	.
$sample_i$	A_{i1}	A_{i2}	.	.	.	A_{in}	S_i
	.	.	.	.	.	.	.
	.	.	.	.	.	.	.
$sample_k$	A_{k1}	A_{k2}	.	.	.	A_{kn}	S_k

In general, the subscripts i refers to samples and j to peak numbers.

Table 4   Peak areas after normalization according to the method NORM

	$peak_1$	$peak_2$	.	.	$peak_n$
$sample_1$	$a_{11}=A_{11}/S_1$	$a_{12}=A_{12}/S_1$	.	.	$a_{1n}=A_{1n}/S_1$
	.	.	.	.	.
	.	.	.	.	.
$sample_i$	$a_{i1}=A_{i1}/S_i$	$a_{i2}=A_{i2}/S_i$	.	.	$a_{in}=A_{in}/S_i$
	.	.	.	.	.
	.	.	.	.	.
$sample_k$	$a_{k1}=A_{k1}/S_k$	$ak2=A_{k2}/S_k$	.	.	$a_{kn}=A_{kn}/S_k$
Avg	Avg_1	Avg_2	.	.	Avg_n
Std	Std_1	Std_2	.	.	Std_n

The average, Avg_j, and the standard deviation, Std_j, of the peaks presented are used for autoscaling.

3.2   Commonly used normalization methods

Normally, each peak area is measured with an absolute error. This error may be positive or negative and will be called the error (E). The error divided by the peak area is called the relative error (E%). In the peak areas obtained after Py-GC analysis the relative error of most peaks is around 7%. However, a few small peaks have a larger relative error. The error therefore, depends on the value of the peak area and is about $A_{ij} * (7/100)$. In this study 27 peaks are taken into account and especially one peak, 1,3-butadiene, is dominant. About 40% of the sum is contributed by 1,3-butadiene. The error in the sum is then particularly determined by the error in this peak. When chromatograms are normalized each peak area is divided by this sum. If the error in 1,3-butadiene is strongly positive the error in the sum is probably positive as well. Then the normalized peak areas of the other peaks are calculated too small and vice versa. In other words, the error in the largest peak is inversely divided over the other peaks. Or in a mathematical way:

$$A_{ij} = Ar_{ij} + E_{ij} \tag{1}$$

A is the measured area, Ar is the real area and E the error. It is assumed that $(E_{ij}/Ar_{ij}) \approx constant$, i.e. the relative error is constant for all peaks. The sum will become:

$$\begin{aligned} S_i &= (Ar_{i1} + ..Ar_{in}) + (E_{i1} + ..E_{in}) \\ &= \Sigma Ar_{ij} + \Sigma E_{ij} \\ &= \Sigma A_{ij} \end{aligned} \tag{2}$$

Normalization gives:

$$\begin{aligned} a_{ij} &= (Ar_{ij} + E_{ij})/S_i \\ &= (Ar_{ij} + E_{ij})/(\Sigma Ar_{ij} + \Sigma E_{ij}) \end{aligned} \tag{3}$$

From equation (3) it can be inferred that the best approximation of a_{ij} is obtained when the error in the sum, ΣE_{ij}, is minimal. The error Eij in A_{ij} is inherent to the Py-GC method.
Another well known normalization procedure is commonly used in mass spectrometry (MSNORM). Mass spectra are normally presented relative to the largest peak. Each peak intensity is divided by the intensity of the largest peak and the resulting mass spectrum is solely affected by the error in one peak. Therefore it is of no surprise that different results can be obtained with PCA after applying this normalization method to various large peaks [8]. When mass spectra are used in multivariate data analysis methods most investigators prefer to use the NORM method [8,9,10].

3.3   Comparison of normalization methods

The effects of the errors, dependent on which normalization method is used, can be studied with a simulated data set which consists of 10 known peak areas and errors. For this set the errors are known and will be referred to as real errors. In Table 5 the real relative errors in column 3 were calculated on the basis of the equation:
(RND - 0.5)*Ar*10%, where RND is a random number between 0 and 1. On average, this implies an error of +/- 5%. The 3 different normalization methods were performed on both Ar and A. The error in the applied method is calculated as: $\{(ar_i - a_i)/ar_i\} * 100\%$.

Table 5   *Comparison of the 3 normalization methods for a simulated data set (error in the largest peak is small)*

no.	Ar	A	real E%	MSNORM E%	NORM E%	NEWNORM E%
1	32000	30809	-3.7	-2.8	-4.7	-4.4
2	900	923	2.7	3.7	1.6	2.0
3	59000	64237	8.9	9.9	7.7	8.1
4	14500	14376	-0.8	0.1	-1.9	-1.5
5	4800	5059	5.4	6.4	4.3	4.7
6	12000	11899	-0.8	0.1	-1.9	-1.5
7	18000	18837	4.7	5.7	3.5	3.9
8	600	619	3.2	4.2	2.1	2.5
9	110	99	-9.7	-8.8	-10.7	-10.3
10	170000	168370	-1.0	0.0	-2.0	-1.6
sum	311910	315231				

Table 6   *Comparison of the 3 normalization methods for a simulated data set (error in the largest peak is large)*

no.	Ar	A	real E%	MSNORM E%	NORM E%	NEWNORM E%
1	32000	34688	8.4	-0.4	2.7	6.6
2	900	959	6.6	-2.1	0.9	4.8
3	59000	59484	0.8	-7.4	-4.5	-0.9
4	14500	13476	-7.1	-14.6	-12.0	-8.6
5	4800	5103	6.3	-2.3	0.7	4.5
6	12000	11288	-5.9	-13.6	-10.9	-7.5
7	18000	18587	3.3	-5.1	-2.2	1.5
8	600	564	-6.0	-13.6	-10.9	-7.5
9	110	116	5.6	-3.0	0.0	3.8
10	170000	185045	8.9	0.0	3.1	7.0
sum	311910	329314				

In the situation when the error in the largest peak (number 10) is small all 3 normalization methods give similar satisfying results. Unfortunately, this will not always be the case. When the error in peak number 10 is large, as shown in Table 6, the NORM and the MSNORM methods produce incorrect results. The worst result is obtained by the MSNORM method. The NEWNORM method produces errors which are very similar in size and sign compared to the real errors. No 'spreading out' effect is observed. It is clear that the problem can be attributed to the errors in the large peaks. The more they are averaged out, the smaller the error in the sum of the peak areas becomes. The errors average out in a better way when they are about equal in size, apart from the sign. When the

relative errors of the peaks are comparable, the errors can be made comparable by means of a transformation of the data A_{ij}. All the original peak areas are transformed to peak areas which have about the same size. This is accomplished by multiplying each peak area by a constant, which is different for each peak, in the following way:

$$A_{ij}.C_j \approx A_{ik}.C_k \qquad \text{with } (j \neq k)$$

Of course, for peak areas which can only be determined with a relative large error, a smaller value of the constant must be chosen to assure that the errors are about equal in size. Applying this concept to eq.(2) gives:

$$
\begin{aligned}
S_i^* &= (Ar_{i1}.C_1 + .. Ar_{in}.C_n) + (E_{i1}.C_1 + .. E_{in}.C_n) \\
&= \Sigma Ar_{ij}.C_j + \Sigma E_{ij}.C_j \\
&= \Sigma A_{ij}.C_j
\end{aligned}
\qquad (4)
$$

The new sum S_i^* is now used in eq. (3) for the normalization procedure. The results are shown in Table 7 using the data from Table 6.

Table 7   Example of the NEWNORM method

no.	Ar	A	error	constant	Ar*	A*	error*
1	32000	34688	2688	1/3	10666	11562	896
2	900	959	59	10	9000	9591	591
3	59000	59484	484	1/6	9833	9914	80
4	14500	13476	-1023	2/3	9666	8984	-682
5	4800	5103	303	2	9600	10206	606
6	12000	11288	-711	1	12000	11288	-711
7	18000	18587	587	1/2	9000	9293	293
8	600	564	-35	20	12000	11285	-714
9	110	116	6	100	11000	11613	613
10	170000	185045	15045	1/20	8500	9252	752
sum	311910	329314	17404		101266	102994	1727

Using the NEWNORM method the sum of the errors is reduced about 10 times. Relatively, this means a reduction of a factor of approximately 3.5. These values improve quickly as the number of peaks increases.

3.4   Comparing autoscaling

Before a PCA is performed on the normalized data, the data set is subjected to an autoscale proce-
dure. From each peak area the mean is subtracted and the results are divided by the standard devia-
tion (see Table 4). As a result each peak is zero centred and has unit variance.

The new normalization procedure has only effect on the averaging effect of the peak areas.
Multiplication of each peak by a constant preserves all the variation as it was in the original data and
has thus no effect on the multivariate normal distribution (MND) of the data before normalization
[11]. After normalization the MND is different which is merely a consequence of the continued ef-
fects of the errors on the peak areas. The only difference is that the averages and standard devia-
tions of the peaks (Avg_j and Std_j) increases or decreases by C_j. The new Avg_j^* and Std_j^* will be-
come:

$$Avg_j^* \;=\; (A_{1j}.C_j/S_1^* + .. A_{kj}.C_j/S_k^*)/k$$

$$=\; C_j.\left\{(A_{1j}/S_1^* + .. A_{kj}/S_k^*)/k \right\}$$

$$=\; C_j.Avg' \tag{5}$$

$$Stdj^* \;=\; \left\{A_{1j}.C_j/S_1^* - Avg_j^* + ... A_{kj}.C_j/S_k^* - Avg_j^*/(k - 1) \right\}^{\frac{1}{2}}$$

$$=\; \left\{C_j.(A_{1j}/S_1^* - Avg_j' + ... A_{kj}/S_k^* - Avg_j')/(k - 1) \right\}^{\frac{1}{2}}$$

$$=\; C_j.Std_j' \tag{6}$$

For the NORM method autoscaling leads to:

$$a_{ij} = (A_{ij}/S_i - Avg_j)/Std_j \tag{7}$$

The calculation for the NEWNORM method is analogous:

$$a_{ij} \;=\; (A_{ij}.C_j/S_i^* - Avg_j'.C_j)/C_j.Std_j' \;=$$

$$=\; (A_{ij}/S_i^* - Avg_j')/Std_j' \tag{8}$$

The equations (7) and (8) differ only with respect to S_i and S_i^*.
In the next Chapter, the NEWNORM method will be applied.

4 RESULTS AND DISCUSSION

4.1 Homogeneity of PBX samples

From a score plot obtained after the analysis of arbitrary chosen samples (see for example Figure 1) it can be seen that the variance in the measurements was considerably. The coefficient of variation, averaged over the first 27 peaks, was about 7%. Part of this variance can be readily explained and is due to the analysis method. Peak areas in chromatograms can normally be estimated with a duplicity of about 3% [12]. A possible cause of the additional variance could well be the inhomogeneity of the PBX samples. To test this presumption a cylinder of the PBX sample R74 which was analysed before [2] was analysed again by cutting 3 additional pieces from the cylinder at different sites, followed by grounding and measuring. The data of the measurements, each in fourfold, were added to the data set of 5 earlier measured samples [2] and PCA was applied to this set. These 5 samples, H23, H24, R63, R74 and R50, are described in Table 1. The results are presented in Figure 1.
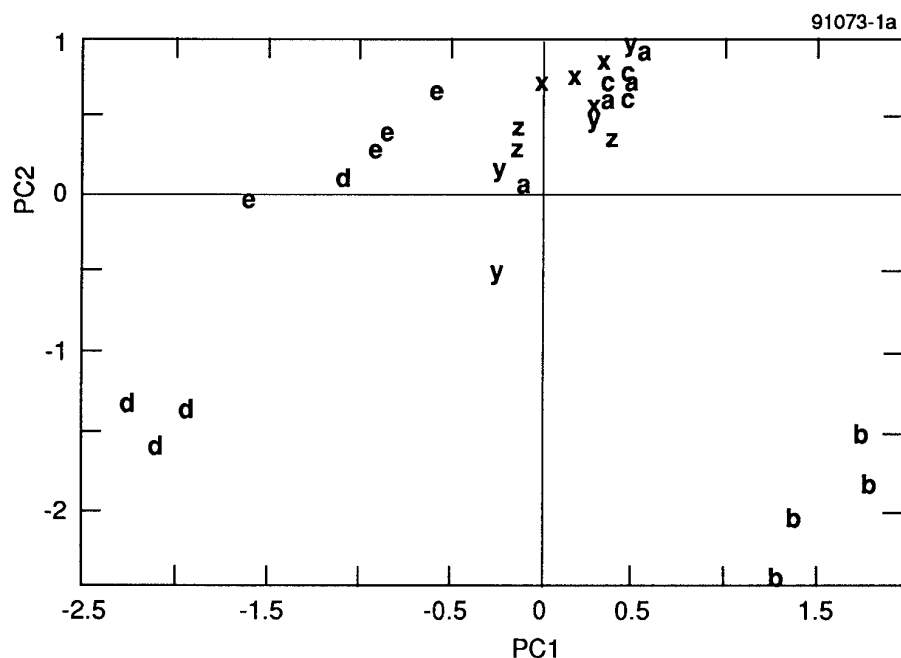

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Figure 1a   Score plot of all analysed samples. PC1 and PC2 explain together 80% of the total variance

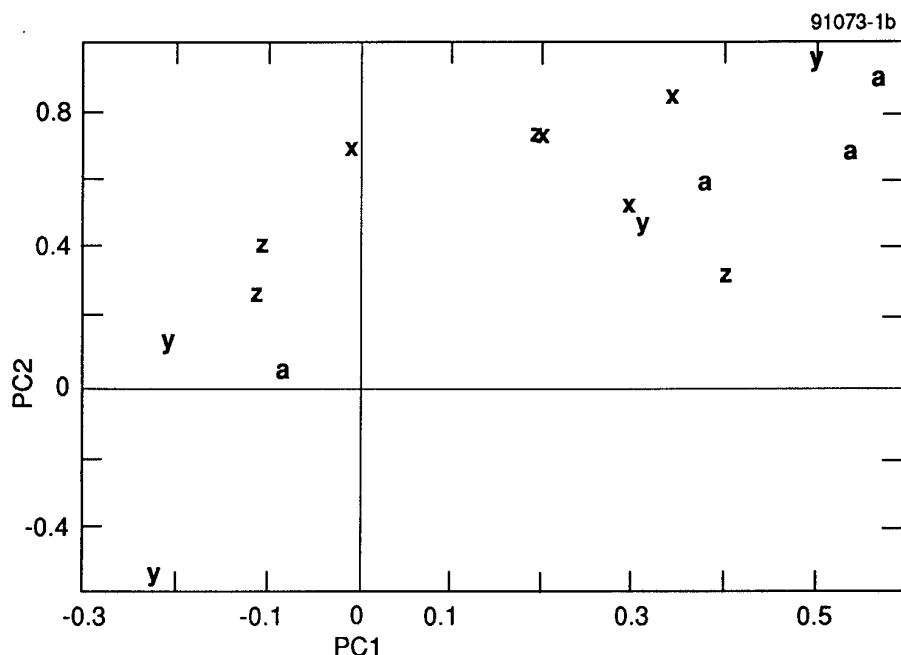|			
a : R74 (piece A)	d : H23	y : R74 (piece C)
b : R50	e : H24	z : R74 (piece D)
c : R63	x : R74 (piece B)	

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Figure 1b   *Detailed score plot of the 4 R74 samples*

In Figure 1b only the cluster representing the sample R74 is depicted. The pieces A and B were cut out from the top of the PBX cylinder, respectively at the centre and at the edge. Piece C was taken at the centre of the middle part of the cylinder and piece D at the bottom between the centre and the edge. The clusters representing each piece are, with the exception of piece C, smaller than the total cluster (Figure 1b). The total cluster is enlarged in the direction of PC1. Most of the peaks have high loadings on PC1 and probably PC1 represents a general degree of variance caused by measurement errors, inhomogeneity and of course large differences between the different samples [13]. A more specific pattern is observed in PC2 which is dominated by the peak numbers 2, 5 and 14. Moreover, the peak nos. 2 and 5 were highly correlated. The pattern in PC3 is less clear and PC4 is represented to a very large extent by peak number 26. Unfortunately, no meaningful interpretation can be given. It is clear that PBX's were not perfectly homogeneous and it is likely that this is also reflected, but in a lesser extent, within each of the pieces A to D.

A possible cause lies in the production of the PBX samples. Before the crosslink agent IDPI is added, the mixture is thoroughly stirred during one hour at 60 °C under vacuum. After the addition of IDPI the total mixture is again stirred for 45 min under the same conditions. Despite these stirring conditions the mixture may still be inhomogeneous. Little or no improvements are to be expected in changing the stirring conditions.

4.2   Effects of antioxidant and crosslink density on aging of PBX samples

Aging of PBX's is caused by the combined effects of oxygen, water, radiation etc. on the samples [14]. Since ground samples are much more exposed to air, it may be expected that these samples age more rapidly. Aging is thought to be proceeded by a radical mechanism initiated by oxygen. The reactive oxygen species is the excited singlet state of oxygen [15,16]. The effect is the formation of additional crosslinks or chain scission in the polymeric matrix. This will result in an increased rigidity of aged PBX's as well as the formation of carbonyl and hydroxyl groups [4,17]. Aging due to reactions between double bonds and the nitramine ($N-NO_2$) groups of RDX or HMX is not very likely [18]. It can, however, not be ruled out that decomposition products of RDX or HMX are responsible for the aging process. In HTPB based propellants containing ammonium perchlorate (AP), the latter is responsible for the aging reaction [4].

4.2.1   Aging of ground samples

To test the influence of air on ground samples and the effectness of added antioxidant (Flexzone), 3 PBX's with different amounts of Flexzone were ground and measured within a time period of 22 days. All samples had the same composition as R74 apart from the content of Flexzone (see Table 1). The crosslink density of the 3 samples was 0.9. Sample A contained no Flexzone, sample B 0.01% and sample C 0.04%. The first measurement was one day after grinding, the second 8 days and the third 22 days. A PCA was performed on the data set containing the results of these Flexzone samples as well as those of the samples described in paragraph 4.2.2 in order to investigate the effect of aging simultaneously. In the plot of PC2 vs. PC1 a certain pattern, in which a separation between the aged and unaged samples is noticed, can be observed (Figure 2). In this score plot only the measurements for the ground samples are shown. On each PC the average scores are depicted. The separation between the aged and the unaged samples lies in the direction of PC1. This separation is additionally reflected in a plot of PC4 vs. PC3. Here, both PC3 and PC4 reflect a separation between aged and unaged samples.
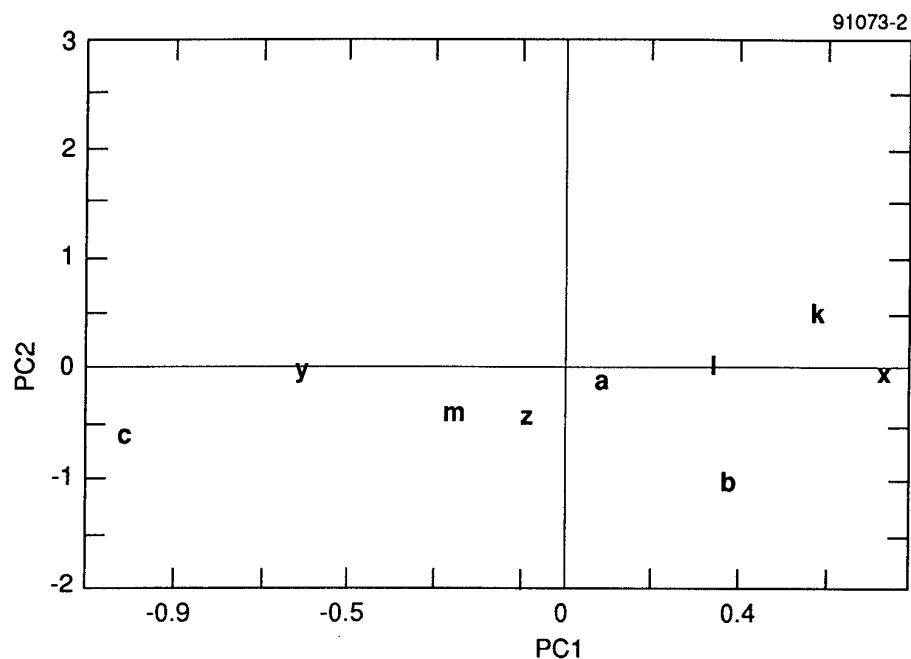
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Figure 2   Score plot of 3 samples with different Flexzone contents

a : 0%, day 1	k : 0.01%, day 1	x : 0.04%, day 1
b : 0%, day 8	l : 0.01%, day 8	y : 0.04%, day 8
c : 0%, day 22	m : 0.01%, day 22	z : 0.04%, day 22

It can be abstracted from Figure 2, that aging depends on the amount of added Flexzone, which is to be expected. Apart from the measurements of sample C8, the change in the pattern of the peaks is less for the samples with the largest Flexzone contents. However, not all the information is presented in this plot. All the available information is used by calculating the distance measures Cosine and the squared Euclidean distance (SED) [2] between the average sample points as performed by the routine 'Cluster' in the SPSS package [19]. The distances are presented in Table 8 with respect to the measurements performed under the normal procedure i.e. after one day.

Table 8   SED and Cosine distances obtained for 3 PBX samples with different Flexzone contents (A:0%, B:0.01% en C:0.04%)

	SED	Cosine
A1 - A8	43	0.12
A1 - A22	82	-0.22
B1 - B8	18	0.73
B1 - B22	61	-0.33
C1 - C8	84	-0.70
C1 - C22	33	-0.36

A decrease in the SED is observed for the samples A and B after longer times. The behaviour of the measurements of sample C8 is peculiar and cannot be explained. The distances as measured for the 22 days periods decrease as the amount of Flexzone in the samples increases. For the Cosine measure these tendencies are much less apparent. However, the changes in both distances confirm the conclusions based on the PCA plot.

4.2.2   Samples with different crosslink densities

Depending on the ratio of IDPI and HTPB, the polymer matrix can be made with a specific crosslink density (CD). Higher ratios (i.e. relative more IPDI) result in more crosslinks and subsequently in a more rigid matrix. The crosslinks are formed by a reaction of the urethane moiety with another molecule of IDPI resulting in an allophane linkage.
A series of 7 PBX samples with CD values ranging from 0.7 up to 1.3 were prepared. The overall composition corresponded with sample R74 (Table 1). These samples with a Flexzone content of 0.01% were measured in fourfold before and after aging. In Table 9 the peak intensities for 5 randomly chosen peaks are listed.

Table 9   Intensities of 5 peaks for unaged and aged (A) samples with different CD values

CD value	peak 1	peak 4	peak 10	peak 13	peak 17
0.7	4703	9314	2039	1708	44855
0.8	4585	8334	1605	1333	35236
0.9	4161	7086	1330	1103	27774
1.0	4558	7309	1349	1135	27099
1.1	4753	7591	1362	1152	26224
1.2	4132	6823	1331	1105	26471
1.3	4742	7500	1365	1127	25381
A0.7	3925	7372	1482	1275	36838
A0.8	4589	7821	1393	1214	30357
A0.9	4884	8560	1267	1124	30518
A1.0	5240	8565	1459	1268	31697
A1.1	4456	7014	1182	1026	25236
A1.2	4960	8241	1285	1141	27675
A1.3	5116	7731	1223	1081	24007

In the unaged samples most peak intensities show a sharp decrease in the direction of larger CD values. After the CD value of 0.9 the peak intensities remain more or less constant. A similar, but less pronounced, effect is noticed for the aged samples. Comparing the aged with the unaged samples, the general decreasing tendency appears to be superimposed with an opposite effect. This applies for all 27 peaks. Thus for peak number 1, whose intensity does not fluctuate largely for the unaged samples, an increase in the aged samples is observed. The large decrease for peak number 17 is turned into a smaller decrease.
It was found by Rao et al [20] that uncured HTPB behaves in a very similar way as the cured polymer. This behaviour was rationalized by the observation that the urethane linkage in cured

HTPB undergoes a reversible cleavage at elevated temperatures forming the alcohol and the iso-cyanate. Uncured HTPB can be considered as a prepolymer with a CD value of zero. The peak intensities originating from the uncured HTPB were slightly larger compared to those from the cured polymer. This is in contrast with the results listed in Table 9. Especially the samples with CD values of 0.7 and 0.8 show a marked enlargement in the intensities for most peaks. The nature of the observed products was independent of the CD value which is in accordance with the findings of Rao et al [20]. As shown in Figure 3, the patterns of the peaks are dependent on the CD value. Unfortunately, no satisfactory explanation of the observed results can be given.

The degradation products studied here are only a subset (smaller hydrocarbons) of the total number of products formed during the pyrolysis. Since the pyrolysis is complete it is therefore possible that for samples with low CD values the degradation proceeds easier due to a more loose structure of the polymer resulting in an increase of the smaller hydrocarbons.

On the data set containing both the results of the aged and unaged samples, as well as those of the Flexzone samples (see paragraph 4.2.1), a PCA was applied. In a plot of PC2 vs. PC1 the same pattern was observed between the aged and unaged CD samples as for the Flexzone samples (see Figure 3). The Flexzone samples are repeated for comparison. Also, the same pattern was observed in a plot of PC4 vs. PC3 for both the Flexzone and CD samples. From these plots it may be concluded that there is no difference in aging between the samples with different CD values. This is confirmed by the results obtained from the distance matrix of which the relevant part is presented in Table 10.
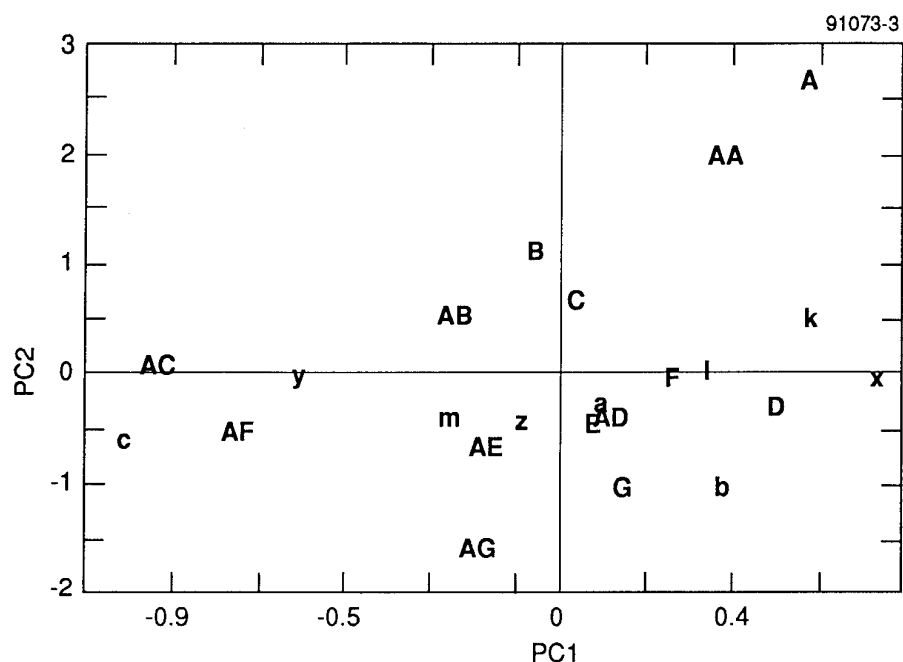
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Figure 3   *Score plot of samples with different CD values and the Flexzone samples. On each PC*
the average scores are shown

	Unaged		*Aged*		*a*	*: 0%, day 1*
A	*: CD 0.7*	*A A*	*: CD 0.7*		*b*	*: 0%, day 8*
B	*: CD 0.8*	*AB*	*: CD 0.8*		*c*	*: 0%, day 22*
C	*: CD 0.9*	*AC*	*: CD 0.9*		*k*	*: 0.01%, day 1*
D	*: CD 1.0*	*AD*	*: CD 1.0*		*l*	*: 0.01%, day 8*
E	*: CD 1.1*	*AE*	*: CD 1.1*		*m*	*: 0.01%, day 22*
F	*: CD 1.2*	*AF*	*: CD 1.2*		*x*	*: 0.04%, day 1*
G	*: CD 1.3*	*A G*	*: CD 1.3*		*y*	*: 0.04%, day 8*
					z	*: 0.04%, day 22*

Table 10   *Calculated distances between the unaged and the corresponding aged samples*

CD value	SED	Cosine
0.7	55	0.59
0.8	26	0.13
0.9	42	-0.03
1.0	14	0.32
1.1	26	-0.04
1.2	47	-0.43
1.3	23	0.69

The numbers in Table 10 seem more or less random and therefore no relation can be inferred about
the stability of the PBX samples and their CD value.

4.2.3   Mechanism of aging

A closer examination of the Figures 2 and 3 learns that the patterns change in a certain direction. This direction is the same for the Flexzone samples as for the CD samples. In a plot of PC4 vs. PC3 the same direction is also noticed. From the unaged to the aged samples this direction is negative both in PC3 and in PC4. It appears that with Py-GC no distinction can be made between samples which are aged in a climate test chamber or naturally aged ground samples. Therefore, it is reasonable to assume that the same mechanism is responsible for aging in both types of samples [4,21].

In another aging study of HTPB based polyurethane [17] no noticeable differences were found when the aging was performed at 60 °C for at least 30 days. However, under aging at 80 °C the carbonyl and hydroxyl groups increased and the butadiene content decreased. The PBX samples studied were aged during 30 days where the highest temperature reached 63 °C. As shown in the PCA plots, differences could be observed applying this aging program indicating that aging took place. The separation can be attributed only to a slight extent to a decrease in butadiene and cis/trans-butene. Other compounds, of which the mechanism of formation is unknown, appeared to be more important in discriminating aged and unaged PBX samples. However, it will be difficult to elucidate the aging mechanism by means of the Py-GC method, since little is understood about the pyrolysis degradation mechanisms despite some studies [20,22,23,24]. In fact, the effects of the aging process and the pyrolysis are examined together.

In order to throw some light on the mechanism of aging a closer look of the loadings will be needed. In Table 11 the loadings are presented for the first 4 PC's, which explain about 87% of the total variance. High loadings reflect a strong contribution of a variable to a PC, whereas the sign indicates the direction of the effect.

Table 11   Component loadings of the data set containing the Flexzone and the CD samples

peak no.	PC1	PC2	PC3	PC4
1	-0.18	-0.83	-0.01	0.25
2	0.48	-0.81	0.05	-0.18
3	-0.85	0.12	0.12	0.38
4	-0.82	0.25	-0.19	0.06
5	0.60	-0.74	0.14	-0.11
6	-0.42	0.64	0.21	-0.37
7	-0.89	0.29	0.08	0.21
8	0.21	-0.86	0.32	0.07
9	0.73	-0.59	0.22	-0.03
10	0.64	0.68	0.18	0.26
11	0.28	0.88	0.20	-0.17
12	-0.49	-0.58	0.44	0.14
13	0.70	0.68	0.09	0.16
14	0.24	-0.76	0.05	-0.21
15	-0.92	0.15	0.06	0.19
16	0.91	-0.23	0.16	0.02
17	0.44	0.77	-0.31	0.14
18	-0.40	0.46	-0.12	-0.69
19	0.73	0.51	-0.12	0.34
20	0.84	0.37	-0.06	-0.19
21	-0.22	0.64	0.62	-0.32
22	0.79	0.54	0.16	-0.13
23	-0.86	0.17	-0.13	-0.02
24	0.36	0.62	-0.31	0.18
25	0.87	0.35	0.14	0.26
26	0.00	-0.32	-0.86	-0.16
27	0.63	-0.44	-0.38	-0.09

Except for PC2 the other PC's were all related to the aging process. For PC1 no specific relationship can be determined between the compounds and the loadings, whereas for PC2 such a relationship can be established. Peak number 26, identified as C_5H_6, has a very high negative loading on PC3. On PC4 peak number 18, cyclopentene, has a high negative loading. For both compounds this means an enhanced peak intensity in aged samples compared to unaged samples. For the Flexzone samples these enhancements become less, especially for C_5H_6, as the samples contain more Flexzone. There was, however, no correlation between the 2 peaks (R ≈ 0.005), which indicates that the formation of these compounds was independent from each other. The tendencies of both compounds can to a lesser extent also be observed in the data set described in paragraph 4.1. In this data set the sample R74 was relative freshly prepared (0.6 years) compared to the other samples (≈ 3.5 years). This strongly indicates that the formation of these 2 compounds is a result of the aging process.

High correlations between a few peaks were observed. The peak nos. 2, 5 and 9 (ethane, propane and n-butane) were all positively correlated (R ≈ 0.98) and were formed in a ratio of 1:2:4 (peak areas). The peak nos. 10 and 13 (trans- and cis-butene), formed in a ratio of 1:1, were also highly correlated (R ≈ 0.98). These high correlations were also noticed in the data set described in paragraph 4.1, except for the correlation of n-butane with propane and ethane. This indicates that the formation of ethane and propane are closely related as well as the formation of trans- and cis-butene. The appearance of ethane and propane as well as trans- and cis-butene in the same propor-

tions was found in aged and unaged samples. However, the peak intensities themselves of trans- and cis-butene showed a decrease towards aged samples, whereas ethane and propane remained about equal.

PC2 is related to saturated compounds (methane, ethane etc.), which have high negative loadings and unsaturated compounds (ethene, acetylene etc.), which have high positive loadings. Samples with low CD values have positive scores on PC2, whereas samples with high CD values have negative scores on PC2 (see Figure 3). Consequently, a polymer with a low CD value produces relatively more unsaturated compounds and vice versa. This can be explained by the fact that polymers with a low CD value are less polymerized and contain therefore more free hydroxyl groups. During pyrolysis these hydroxyl groups eliminate water. The remaining polymer will then become more unsaturated. Furthermore, high loadings of the peak nos. 1, 8, 11 and 14 were only found on PC2. Peak nos. 1, 8 and 14 have a negative loading whereas peak number 11 has a positive loading. Since the peak nos. 1 and 11 (methane and 1-butene) had the largest negative correlation, the ratio of both peaks was correlated with the crosslink density. This resulted in a straight line with a positive coefficient for the CD values 0.7 up to 1.0. Above a value of 1.0 the coefficient became zero. This is explainable since above a CD value of 1.0 there are almost no free hydroxyl groups left in the polymer because HTPB and IDPI are present in equivalent proportions.

4.3   PBX samples from other nations

From 2 other nations, the UK and Norway, PBX samples were analysed. The 3 Norwegian samples contained large cavities which was due to the fact that the constituents were not mixed under vacuum. In comparison with the Dutch and the UK samples the Norwegian samples contained large RDX crystals, which gave the samples a granular appearance. Since with Py-GC the overall composition is examined it is unlikely that these deviations have influence on the pattern of the peaks. From the UK a lot of small samples were received. These samples were too small in size to treat them according to the developed method [2]. It was impossible to cut the edges from the samples, which had been in contact with the polymer packaging material, and be left with an 1 g PBX sample. The largest sample was treated with the standard procedure as good as possible. Both the edges and the inside of the sample were analysed in order to see whether there were differences between these parts. The sample with the edges cut off was labelled U and the edges themselves U*. Possible differences could be due to contamination of the sample by substances, for example the plasticizer, of the polymer packaging material.

The samples from Norway were large enough to test them on inhomogeneity. Two blocks were produced by a continuous process and were labelled NC. One block was obtained from a batch process and was named NB. From each of the 3 blocks 2 samples were taken. Each sample was measured in fourfold. The Dutch samples were labelled 'A' to 'E' as in paragraph 4.1. In Table 1 the compositions of the samples are described.

On the data set containing the data of the samples from the 3 nations a PCA was applied of which the results are shown in Figures 4 and 5. In Figure 4 all samples are spread out more or less in a random way. A difference between the samples could, however, be found in a plot of PC4 vs. PC3 (Figure 5). This indicates that there were differences but that these were subtle. They are probably not caused by the amount and type of the plasticizer used. The analysis of the 2 plasticizers IDP and DOP (di-octylphthalate) showed that the GC-patterns were very much alike up to a retention time of 11 minutes. Clearly, further research will be needed to reveal the differences between the samples from the 3 nations.
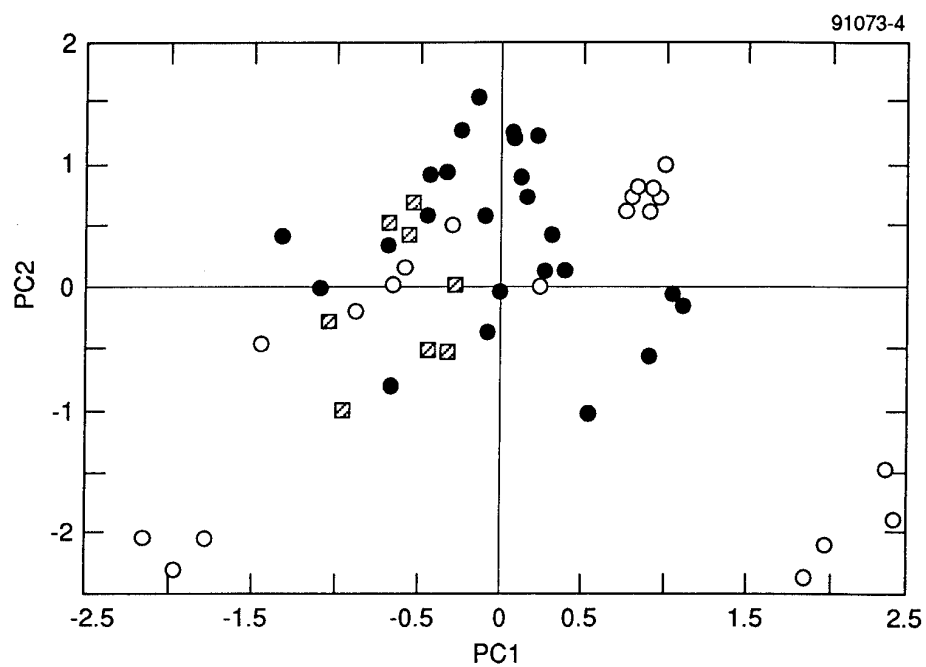
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Figure 4   Score plot of PC2 vs. PC1 of the UK (▨), Norwegian (●) and Dutch (○) samples
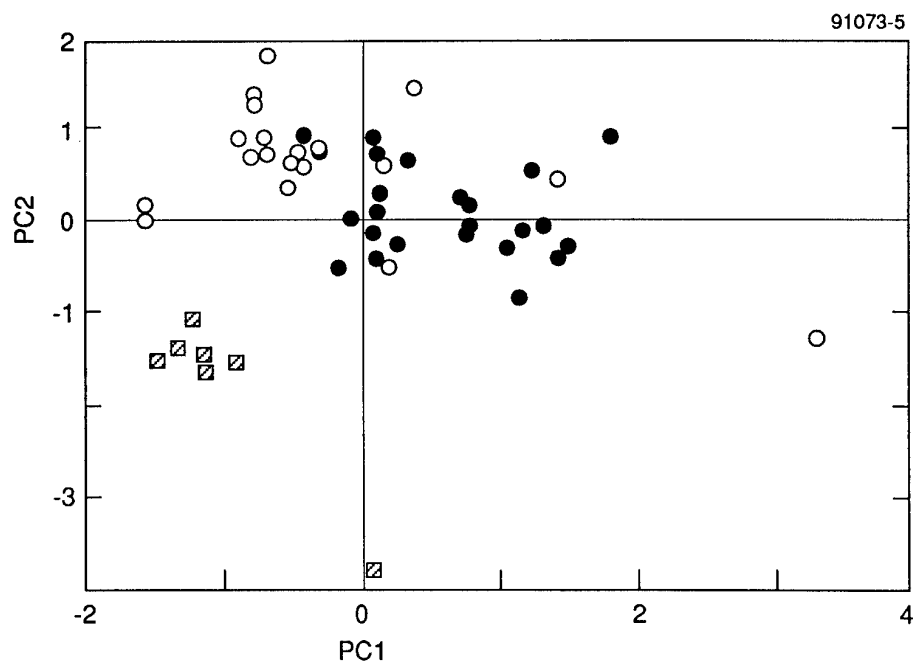
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Figure 5   Score plot of PC4 vs. PC3 of the UK (▨), Norwegian (●) and Dutch (○) samples
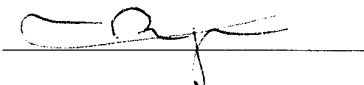
5 CONCLUSIONS

The procedure for the characterization of PBX samples by Py-GC and PCA was further improved by developing a new normalization method of the GC-peak areas. It was demonstrated with the improved procedure that:
- PBX samples were inhomogeneous.
- Aging of ground samples depended on the amount of added antioxidant.
- Differences could be made between samples with a low and a high crosslink density.
- Aging of samples with different crosslink density values proceeded in the same way.
- Aging in a climate test chamber proceeded in the same way as the natural aging of ground samples.
- Samples from 3 nations showed small differences.

Further testing of the procedure will be needed to explore its possibility as a quality control method.

6 AUTHENTICATION

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Applications of the developed procedure based on pyrolysis-gas chromatography (Py-GC) and principal component analysis (PCA) for the characterization of plastic bonded explosives (PBX's) are described. Due to difficulties with the commonly used normalization method a new normalization method was developed and applied in this investigation. The patterns in the score plots obtained after PCA of the Py-GC results appeared much clearer using this new method. PBX samples were examined on homogeneity, influence of the amount of antioxidant (Flexzone) and the crosslink density. It appears that PBX's were inhomogeneous despite a thorough mixing of the constituents during the preparation. Aging experiments were performed on samples which differed in the amount of Flexzone and in the crosslink density. As more Flexzone was added the change in the pattern of the GC-peaks became less. No relation could be found between the stability of PBX's and the crosslink density. Finally, a comparison was made between Dutch samples and samples from the UK and Norway. Small differences were observed between the samples from the three nations.

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